ANTIMONY SILICATE SORBENT FOR REMOVAL OF METAL IONS

Cross-Reference To Related Applications

[0001]   This application is a divisional of USSN 09/674,596 filed February 27, 2001, which was an application under 35 U.S.C. 371 based on PCT application number PCT/GB99/01305, hereby incorporated by reference.

Field of the Invention

[0002]   The present invention relates to the removal of metal ions from a solution phase. As an example, it may be used in the removal of radionuclides from a solution, but it should be understood that the invention is not restricted in any way to radionuclides.

Background of the Invention

[0003]   In the nuclear industry large volumes of aqueous streams are produced which contain radionuclides and other polluting metal species. It is desirable to dispose of such wastes with minimum volume for maximized capacity usage. Actinide elements, fission products, activation products and heavy metals typically are removed from such wastes. Techniques such as flocculation or ion exchange have been employed to remove these species and have been generally successful. However, certain radionuclides can be more problematic to remove than others. For example, strontium ions are difficult to remove by known ion exchange techniques when present in acidic media. Moreover, other ions present in the solution, eg Ca^{2+}, Mg^{2+}, Na^+, K^+, may interfere with the uptake of strontium. Commercially available materials for Sr removal includes

clinoptilolite (a zeolite mineral), sodium titanates (Allied Signal, US), titanosilicate CST (UPO, US) and titanium-oxide based SrTreat (Selion OY, Finland) which work more efficiently in neutral/alkaline media.

Statement of the Invention

[0004]   According to a first aspect of the present invention, there is provided a use of a material comprising antimony silicate as a sorbent in the removal of metal ions from an acidic liquid medium.

[0005]   The metal ions may be radioactive metal ions.

[0006]   The radioactive metal ions may comprise Sr, Cs, Co, Pu or Am ions.

[0007]   The radioactive metal ions may be removed from an acidic liquid medium which contains background ions such as Na, K, Mg, and Ca ions at a higher concentration than the concentration of the radioactive metal ions.

[0008]   The radioactive metal ions may be selectively removed from the acidic liquid medium which contains background ions such as Na, K, Mg, and Ca ions, the background ions being left behind in the liquid medium.

[0009]   According to a second aspect of the present invention, there is provided a method of preparation of a material comprising antimony silicate, the method comprising reacting together in a liquid medium silicon containing compound and an antimony containing compound under polymerisation conditions, characterised in that the mole ratio of Si:Sb is less than about 20 and the reaction product is dried at a temperature from 40°C to 800°C to form the material.

2

[0010]   Preferably, the reaction product is dried at a temperature from 40°C to 300°C. More preferably, the product is dried at a temperature from 40°C to 100°C.

[0011]   According to a third aspect of the present invention there is provided a method of extracting metal ions from an aqueous solution comprising contacting the aqueous solution with a material comprising antimony silicate prepared by the method of the second aspect of the present invention.

[0012]   The ions may be radioactive ions. The ions may be strontium ions. The aqueous solution may have a pH less than 7.

[0013]   It has been found by the inventors that the material comprising antimony silicate is highly effective as an ion exchange material for selectively removing metal ions, e.g. Sr, Co, Pu and Am ions, from aqueous solutions.

[0014]   The material is effective at selectively removing the metal ions Sr, Co, Pu and Am from a solution containing background metal ions such as Na, K, Mg and Ca whilst leaving behind the background ions in solution.

[0015]   Antimony silicate has been found to be particulary effective at removing radioactive ions. The radioactive ions may comprise one or more of Sr, Cs, Co or Pu metal ions. Also toxic heavy metal ions may be removed.

[0016]   The material has been found to be of comparable effectiveness to commercially available ion exchange materials for the removal of many ions and has been found to be much more effective than

commercial materials for the removal of some ions in particular. The material is more efficient at removing Sr, Co, Pu and Am ions, for example, than many conventional ion exchanges. The material is very effective at removing Sr ions from aqueous solution.

[0017]   The material has been found to be especially good at removing Sr ions from acidic media. In contrast, known ion exchangers are poor at removal of metal ions, in particular Sr, from acidic aqueous media.

[0018] K_d values for several nuclides in various 'model' test media are shown in Table 1. K_d is calculated according to equation 1.

$$K_d=(Ai-A).V/Ai.m \qquad (1)$$

where Ai is the initial cation concentration, A is the cation concentration after contact with the ion exchanger, V is the volume of solution and m is the mass of the ion exchange material. K_d is an estimation of the processing capacity of the material. K_d is a measure of the distribution of the isotope between the solid and liquid phases.

[0019]   The material is much more efficient for Sr uptake, for example, than commercial materials such as CST and clinoptilolite, see Figure 2 and Tables 1, 2 and 3.

[0020]   The material is also more efficient for Sr uptake than commercial materials in the presence of other cations such as Na^+ for example, see Figure 7.

[0021]   The material may be amorphous or crystalline but is preferably crystalline. Preferably, the X-ray Diffraction (XRD) pattern of the crystalline material shows characteristics of crystalline antimony silicate.

[0022]   Referring to the method of preparation of the antimony silicate, the silicon and antimony containing compounds may be compounds which have been used previously such as in J. Solid State Chem., 99, 173 (1992) to synthesise antimony silicates. For example, the silicon containing compound may be $Si(OC_2H_5)_4$ (TEOS) or $Na_2Si_3O_7$ (sodium silicate) or another suitable starting material. The silicon containing compounds may be provided dissolved in a suitable solvent such as water or ethanol for example. The antimony containing compound may, for example, be $KSb(OH)_6$ or $SbCl_5$. The antimony containing compound may be dissolved in water or other suitable solvent. Preferably the antimony containing compound comprises Sb(V) rather than Sb(III).

[0023]   The Si:Sb mole ratio is less than about 20. Preferably the Si:Sb mole ratio is less than 5. More preferably, the Si:Sb ratio is in the range from 3:1 to 1:3. Most preferably the Si:Sb ratio is from 1:1 to 1:2.

[0024]   The reaction product may be dried for a period of time of, e.g., several days. The reaction product may be dried for an overnight period. The reaction product is dried at a temperature from slightly above ambient temperature to about $800°C$. Particularly, the drying temperature is from $40°C$ to $800°C$. Preferably, the drying temperature is from $40°C$ to $300°C$. More preferably, the drying temperature is from $40°C$ to $100°C$. Typically, the reaction product may be dried for an overnight period at a temperature from about $40°C$ to about $70°C$.

[0025]   Figure 8 shows how the distribution coefficient, Kd, value for [85]Sr varies according to the drying temperature used.

[0026]   The compounds may be reacted together by mixing them. The mixing time may vary, for example from about an hour to several days. Preferably the mixing time is from one to eight hours. The mixing time may however be much shorter or much longer than the time given as an example.

[0027]   The polymerisation conditions may be provided by the presence of a suitable polymerisation catalyst such as, for example, an acid. The acid may be, for example, HNO_3, HCl or H_2SO_4. The acid may be added to the antimony containing compound before the silicon containing compounds is added or after.

[0028]   The reaction product may be filtered and/or washed with water at one or more stages before or during the drying.

[0029]   According to a fourth aspect of the present invention there is provided a material comprising antimony silicate doped with one or more elements selected from the group consisting of tungsten, niobium and tantalum.

[0030]   The material according to the fourth aspect may be referred to hereinafter as the doped material. The one or more elements selected from the group consisting of tungsten, niobium and tantalum may be referred to hereinafter as the dopant species.

[0031]   According to a fifth aspect of the present invention there is provided a use of a material comprising antimony silicate doped with one or more elements selected from the group consisting of tungsten, niobium and tantalum as a sorbent in the removal of metal ions from a liquid medium.

6

[0032]   According to a sixth aspect of the present invention there is provided a method of extracting metal ions from an aqueous solution comprising contacting the aqueous solution with a doped material according to the fourth aspect of the present invention.

[0033]   The doped material may be doped with only one element from the group consisting of tungsten, niobium and tantalum. The doped material may be doped with two or more elements from the group consisting of tungsten, niobium and tantalum.

[0034]   Tungsten and/or niobium are the preferred dopant species.

[0035]   The mole ratio of Sb:Si:dopant may be in the range from about 1:1:0.005 to about 1:1:2, for a case where the Sb:Si ratio is about 1:1. Generally, better results are obtained where the dopant level, Sb:Si:dopant, is from about 1:1:0.01 to about 1:1:0.5. However, the optimum dopant level may not always fall in the forgoing range as other factors such as the Si:Sb ratio, the type of synthesis reagents, drying times and temperatures may affect the optimum dopant level. Also, the optimum dopant level will depend on the type of ion to be removed from solution.

[0036]   Preferably, the weight % concentration of the dopant in the material should be in the range from about 0.5 to about 30.0 weight %. The precise optimum dopant level will depend, inter alia, on the ion to be removed from solution. Some optimum tungsten dopant levels for various ions are shown in Figure 13.

[0037]   The doped material may be crystalline or amorphous in structure. A crystalline structure is preferred. The XRD pattern of the

crystalline structure preferably is substantially similar to the XRD pattern of crystalline antimony silicate.

[0038] It has also been found that doping an antimony silicate with one or more elements selected from the group consisting of tungsten, niobium and tantalum changes the selectivity for different ions. Thus, selective doping with the aforementioned dopants may be controlled in a way so as to make antimony silicate more selective towards particular metal ions. For example, it has been found that doping with W can lead to greater selectivity for caesium ions.

[0039] According to a seventh aspect of the present invention there is provided a method of preparation of a material comprising antimony silicate doped with one or more elements selected from the group consisting of tungsten, niobium and tantalum, the method comprising reacting together in a liquid medium a silicon containing compound, an antimony containing compound and a compound containing the one or more elements under polymerisation conditions.

[0040] The method according to the seventh aspect of the invention includes the features and options of the method according to the second aspect of the invention for preparing an antimony silicate where applicable.

[0041] The fourth, fifth, sixth and seventh aspects of the present invention include the options and features of the first, second and third aspects where applicable.

[0042] Specific embodiments of the present invention will now be described by way of the following examples. The examples are illustrative only and do not limit the invention in any way.

[0043] <u>Examples</u>

[0044] (1) <u>Basic Preparation</u>

[0045] Antimony silicates were prepared by the following two methods.

[0046] <u>Method A</u>

[0047] 5.26_g of $KSb(OH_6)$ was dissolved in 360 ml distilled H_2O and this was then added under stirring to 4.17g of TEOS dissolved in ethanol. 2.75ml concentrated $HN0_3$ was then added as polymerisation catalyst, and the mixture stirred for 1 hour at 77°C. The product was washed with distilled water and dried. The dried product was then heated to form the desired material. The materials were found to be amorphous under XRD analysis (see Figure 1). Table 1 shows the Kd values for various ions for a sample which was heated to 450°C.

[0048] <u>Method B</u>

[0049] $SbCl_5$ was mixed with sodium silicate, $Na_2Si_3O_7$, in the presence of 4M HCl with the pH maintained at about 1. This formed a gel-like product after being left at $60^{\circ}C$ overnight. The product was filtered and washed and dried and the XRD trace showed that the material was crystalline.

[0050] The results described below were obtained using the material prepared by method A above.

[0051] (2) <u>Effect of pH and co-present metal ions</u>

[0052] Figures 2 and 3 shows how the K_d value for ^{85}Sr varies as a function of pH in 0.1M $NaNO_3$ for the antimony silicate prepared at

9

450°C as above, commercial CST and clinoptilolite and the commercially available SrTreat material. The Kd values for the antimony silicate are almost constant between pH3-13 and Kd is still above 1000 ml/g at pH 1 which is far superior to the commercial SrTreat and CST and clinoptilolite.

[0053]   Figure 4 shows how the K_d values are affected by the presence of calcium ions.

[0054]   Figure 5 shows how the K_d values are affected by the presence of Mg^{2+} ions.

[0055]   Figure 6 shows how the K_d values are affected by the present of K^+ ions.

[0056]   Figure 7 shows how the K_d values are affected by the presence of Na^+ ions.

[0057]   (3)   Effect of Synthesis Temperature

[0058]   Different antimony silicate samples were then prepared by heating the product to various temperatures. Samples were prepared by heating to 100°C, 200°C, 300°C, 450°C, 600°C and 800°C. Figures 8 and 9 shows how K_d for ^{85}Sr and ^{57}Co varies with the synthesis temperature. A slight maximum is seen at about 300°C. Separate results are given for the case when acid is added in the synthesis before the silicate (see below).

[0059]   (4)   Effect of Adding Acid before Silicate

Samples were prepared as above with various synthesis temperatures except that some HNO_3 was added before TEOS to hasten the solubility of the $KSb(OH)_6$. The comparison of the Kd values with and without prior addition of HNO_3 are shown in Figures 8 and 9. The material prepared

10

where the acid was added before the silicate was slightly better at removing ^{85}Sr and ^{57}Co.

[0060] (5) <u>Effect of Sb:Si ratio</u>

Synthese were also carried out in which the Sb:Si ratio was varied. The Sb:Si ratios used were 1:1, 2:1, 3:1, 1:2 and 1:3. Also a synthesis was carried out without any silicate to produce antimonic acid. They synthesis temperatures were about 100°C and 300°C. The K_d values for ^{85}Sr in 0.1M HNO$_3$ are shown in Figure 10.

[0061] Antimonic acid and the Sb:Si=1:2 showed the best performance. When the amount of Sb is increased the K_d values for ^{85}Sr tend to fall. The ratio of Sb:Si giving the best performance for Sr removal was found to be 1:1 to 2:1.

[0062] (6) <u>Preparation of Tungsten doped Antimony Silicate</u>

[0063] <u>Method A</u>

[0064] Na$_2$WO$_4$·2H$_2$O was mixed with KSb(OH)$_6$ and TEOS at acidic pH in Sb:Si:W mole ratios of 1:1:0.5, 1:1:1, 1:1:2 and 1:1:0.1. The mixtures were kept in a 77°C oven overnight and a gel-like product was filtered and dried at room temperature. The materials so obtained were amorphous when analysed by XRD.

[0065] <u>Method B</u>

[0066] A crystalline tungsten doped material was obtained by adding 6.10g SbCl$_5$ in 100 ml 4M HCl to a solution of 4.46$_g$ sodium silicate ("water glass") in 100 ml water simultaneously with a solution of 3.30g Na$_2$WO$_4$·2H$_2$O in 100 ml water. Additional 200 ml of water was quickly added. Several different Sb:Si:W ratios were used and the

heating time at 77°C was varied. The XRD patterns were characteristic of crystalline antimony silicate.

[0067] (7) <u>K_d Values for Tungsten doped Antimony Silicates</u>

[0068] Table 4 shows K_d values for removal of Cs, Sr and Co in 0.1M HNO_3 using tungsten doped antimony silicates prepared by both methods A and B above.

[0069] For Sr, the K_d values show little improvement over the undoped antimony silicate material, except at very low W levels, eg. Sb:Si:W = 1:1:0.1.

[0070] For Cs removal on the other hand, the K_d values tend to increase with increasing W concentration before decreasing at higher W concentrations. The W doped materials are generally more selective towards Cs than the undoped material.

[0071] Figures 11 a, b, c show how the K_d values change as a function of pH in 0.1NaNO$_3$.

[0072] Figure 12 shows how the K_d value for Sr changes as a function Ca(NO$_3$)$_2$ concentration.

[0073] Figure 13 shows how the K_d values for Cs, Sr and Co change as a function of the weight % loading of tungsten in the material.

[0074] (8) <u>Niobium Doped Antimony Silicates</u>

[0075] To produce a Si:Sb:Nb = 1:1:0.48 material, 0.892g sodium silicate solution (27% SiO_2, 14% NaOH) was diluted to 80 ml with distilled water. This was quickly added to a stirred solution of 1.22 g $SbCl_5$ and 0.53g $NbCl_5$ in 4M HCl (20ml). The resulting clear colourless solution was left overnight at ambient temperature, 348K or 473K. The

products were isolated by centrifugation, washed with distilled water and air dried at 348K. Further samples with different Si:Sb:Nb ratios were made.

[0076]   (9)   K$_d$ Values for Niobium doped Antimony Silicates

[0077]   Table 5 shows K$_d$ values for Cs, Sr and Co in 0.1 M HN0$_3$ for niobium doped antimony silicates prepared at different mole ratios and temperatures.

[0078]   For Cs ions, peaks in the K$_d$ values occur when the Nb:Sb ratio is in the range 0.01 to 0.05 when a synthesis temperature of 298 K is used. When a synthesis temperature of 473 K is used, however, the peak K$_d$ occurs around a Nb:Sb ratio of about 1:1.

[0079]   For Sr ions maximum K$_d$ values are generally seen for low concentrations of Nb.

[0080]

Table 1. Distribution coefficients (K$_D$) for Antimonysilicate

NUCLIDE	4 M HNO$_3$	0.1 M HNO$_3$	0.1 M NaNO$_3$	0.1 M NaNO$_3$ / 0.1 M NaOH	Dist. H$_2$O
Cs-134	32.8	590	280	26.0	2517
Sr-85	68.0	19660	44305	56070	13480
Co-57	—	1959	33807	6177	273
Am-241	3.43	134856	245071	120482	979
Zn-65	2.92	4604	39853	25827	962
Fe-59	—	14292	6442	—	114
Mn-54	—	569	2545	3330	972
Pu-236	17024	14067	8752	417	85.7

— Not measured

[0081]

Table 2 Distribution coefficients (K$_D$) for CST

NUCLIDE	4 M HNO$_3$	0.1 M HNO$_3$	0.1 M NaNO$_3$	0.1 M NaNO$_3$ / 0.1 M NaOH	Dist. H$_2$O
Cs-134	1327	51460	97500	10710	177800
Sr-85	0.60	9.6	1091	465500	18910
Co-57	0.57	0.18	334	1155	26220
Pu-236	12.1	285	31950	9157	789
Am-241	4.35	95.3	18822 !	8577	59388 !

13

[0082]

Table 3 Distribution coefficients (K_D) for clinoptilolite

NUCLIDE	4 M HNO_3	0.1 M HNO_3	0.1 M $NaNO_3$	0.1 M $NaNO_3$ / 0.1 M NaOH	Dist. H_2O
Cs-134	43.0	2524	1844	594	72010
Sr-85	0.5	34.0	422	354	146360
Co-57	1.23	4.05	5777	1310	14360
Pu-236	0	1021	2517	26700	1147
Am-241	0 !	3.78	10435	48874 !	1365

Table 4

Sample name	Starting materials	Sb:Si:W ratio (%) (weight %)	Sb:Si:W mole ratio	XRD trace	K_D(Cs-134), [ml/g] in 0.1 M HNO$_3$	K_D(Sr-85), [ml/g] in 0.1 M HNO$_3$	K_D(Co-57), [ml/g] in 0.1 M HNO$_3$
					Kd/Kd aged 6 days	Kd/Kd aged 6 days	Kd/Kd aged 6 days
1	SbCl$_3$ in 4M HCl, Crystal 0503, Na$_2$WO$_4$·2H$_2$O	59 : 11 : 0	1:~1:0	Cryst. SbSi	12404 / 36307	584512 / 605345	1995 / 12045
2	."..	56 : 11 : 2.4	1:~1:0.03	Cryst. SbSi	18085 / 44951	554420 / 884736	3453 / 33704
3	."..	53 : 11 : 8	1:~1:0.1	Cryst. SbSi	35714 / 86392	230668 / 459068	2263 / 33786
4	."..	46 : 10 : 18	1:~1:0.3	Cryst. SbSi	36472 / 126010	28612 / 49965	1874 / 10841
5	."..	42 : 9.4 : 23	1:~1:0.5	Semicryst. SbSi	16797 / 63573	16644 / 20876	512 / 3033
6	."..	38 : 8.6 : 30	1:~1:1	Amorphous	14602 / 30172	8956 / 8802	379 / 581
7	."..	16 : 5 : 54	1:~1:3	Amorphous	940 / 1039	71 / 69	19 / 108
9	."..	0 : 8 : 71	0:~1:1	Tungstite WO$_3$· xH$_2$O	9244 / 77581	23 / 61	4.5 / 87
10	."..	52 : 3.5 : 25	3:~1:1	Semicryst. SbSi	9812 / 55016	5860 / 13642	179 / 1225
11	."..	------ (1:0:1)	1:0:1	Amorphous	3432 / ---	1108 / ---	154 / ...
12	."..	27 : 21 : 16		Cryst. SbSi	20388 / 45026	23728 / 3706	719 / 533

0084]   Table 5. Distribution coefficients (L/Kg) of Cs-137, Sr-90

and Co-57 in 0.1 mol/L HNO3 on niobium-doped antimony silicates

prepared at different temperatures (V:m=200)

Temp (K)	Starting Si:Sb:Nb	Cs-137	Sr-90	Co-57
298	1:1:0.012	87633	323369	12042
	1:1:0.026	97476	236791 ·	11397
	1:1:0.093	71503	177655	6724
	1:1:0.0263	11014	74176	817
	1:1:0.48	989	745	38
	1:1:0.98	374	37	2
	0.5:1:0.01	54708	627533	21153
348	1:1:0.012	22406	160147	1477
	1:1:0.026	25771	144125	1748
	1:1:0.093	26606	303250	2176
	1:1:0.0263	24990	108549	864
	1:1:0.48	9636	70236	177
	1:1:0.98	637	539	17
	0.5:1:0.01	24556	620052	3240
473	1:1:0.012	5349	43503	2367
	1:1:0.026	6249	14761	1542
	1:1:0.093	3619	15683	4588
	1:1:0.0263	13155	27277	17068
	1:1:0.48	14688	7988	5031
	1:1:0.98	118552	4354	403
	0.5:1:0.01	17550	14451	2772